

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
19 July 2001 (19.07.2001)

PCT

(10) International Publication Number
WO 01/51496 A1

(51) International Patent Classification⁷: C07F 9/30, 9/53, D06M 13/285

(21) International Application Number: PCT/US01/00788

(22) International Filing Date: 10 January 2001 (10.01.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/176,156 14 January 2000 (14.01.2000) US

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(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— with international search report

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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(54) Title: **CROSSLINKING AGENTS FOR TEXTILE FINISHING BATHS**

(57) Abstract: Phosphinato-substituted propane- and butanepolycarboxylic acids and derivatives thereof are useful as crosslinking agents for cellulosic materials to render them wrinkle resistant and/or iron free in a durable press process.



WO 01/51496 A1

CROSSLINKING AGENTS FOR TEXTILE FINISHING BATHS

Field of the Invention

This invention relates to novel crosslinking agents for use in finishing baths for textiles and to a process for finishing textiles to render the textiles wrinkle resistant and/or iron free.

Background of the Invention

Cellulosic fabrics or textile materials are presently generally rendered wrinkle resistant or iron free in a process known as the cotton durable press process (DP process). In such a DP process, cellulosic fabrics are treated in a finishing bath with one or more finishing agents, generally to crosslink the cellulose molecules. Such crosslinking of the cellulose imparts to the fabric a tendency to return to its original shape and smoothness.

Formaldehyde, formaldehyde derivatives and formaldehyde addition products with urea, carbamate esters and other amidic compounds have been extensively used in the past as the crosslinking agents in such a process. However, serious drawbacks or problems have been found to exist with the use of such formaldehyde-derived crosslinking agents, particularly due to the release of dangerous and toxic formaldehyde vapors during the DP process and during subsequent manufacture, use, sale, laundry, and storage of garments made from such crosslinked fabric. In fact, regulations in various countries limit the dose of exposure of formaldehyde to which one can be exposed to a very low dosage amount, and for the

most part effectively limit or prevent the use of such formaldehyde derivatives in the process.

5 In an attempt to avoid the use of formaldehyde or formaldehyde-derived crosslinking agents, several other crosslinking agents have been suggested. For example, in PCT Application No. PCT/US89/02628 (WO 89/12714) of the US Department of Agriculture, there is a proposal to use organic polycarboxylic acids as crosslinking agents with hypophosphite, phosphite or polyphosphate curing catalysts to render cellulosic textile materials wrinkle free. Also, US Patent No. 5,300,240 and
10 EP 0 976 867 A1 disclose that phosphinicosuccinic acid, phosphinobissuccinic acid, or mixtures thereof can be used as crosslinking agents for cellulosic textile materials to render them wrinkle resistant.

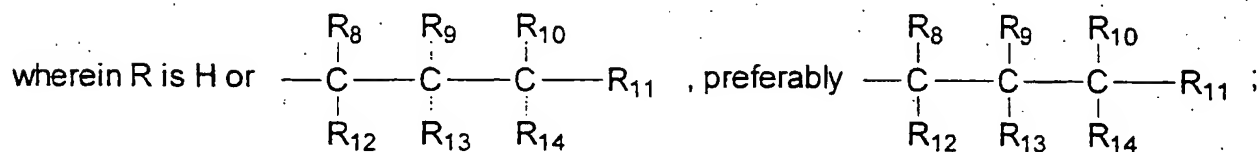
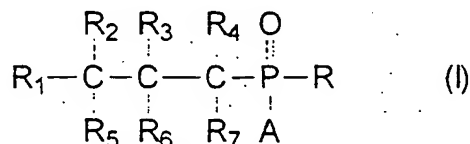
15 However, there is still a need for other cellulosic crosslinking agents for rendering cellulosic textile materials wrinkle resistant that do not release formaldehyde vapors and yet provide wrinkle resistance to the cellulosic material that is as good as that provided by formaldehyde-derived crosslinking agents. Further, there is a need for other non-formaldehyde derived crosslinking agents that function better as cellulosic crosslinking agents than replacement crosslinking agents heretofore proposed.

Summary of the Invention

20 It has been discovered that certain phosphinato-substituted polycarboxylic acids, and suitable salts thereof, function as superior crosslinking agents for cellulosic textile materials or fabrics. The phosphinato-substituted polycarboxylic acid cellulosic crosslinking agents of this invention are phosphinato-substituted propanetricarboxylic acids, phosphinato-substituted butanetetracarboxylic acids, oligomers thereof and mixtures thereof. Also, mixtures of the foregoing with phosphonato-substituted
25 derivatives of these polycarboxylic acids can also be employed as crosslinking agents in a DP process for rendering cellulosic materials wrinkle resistant and iron free.

Detailed Description of the Invention and Preferred Embodiments

The phosphinato-substituted alkanepolycarboxylic acids and salts thereof useful for crosslinking cellulosic materials, especially in a DP process, comprise compounds of the formula (I) and oligomers thereof



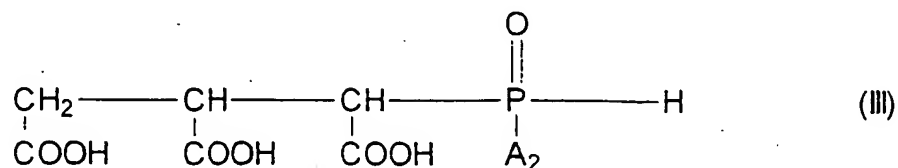
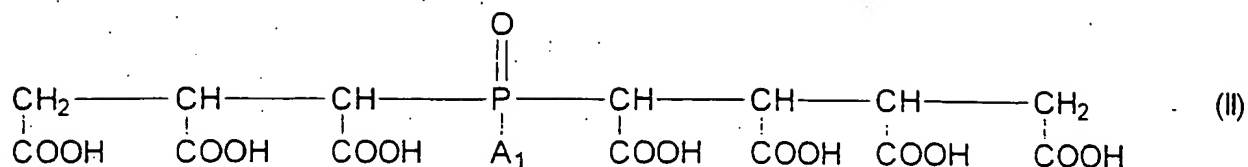
R_1 and R_{11} are each independently H, C_1 to C_4 alkyl or $-CH_2COOM$ in which M is H, Na, K or NH_4 , preferably R_1 and R_{11} are H or $-CH_2COOM$ in which M is H or Na;

R_2 , R_3 , R_4 , R_8 , R_9 and R_{10} are each independently H or C_1 to C_4 alkyl, preferably H;

R_5 , R_6 , R_7 , R_{12} , R_{13} and R_{14} are each $COOM_1$ in which M_1 is H, Na, K, or NH_4 , preferably H or Na; and

A is OH, H, C_1 to C_8 alkyl, cyclohexyl, aryl or OM_2 in which M_2 is H, Na, K or NH_4 , and A is preferably OH or Na.

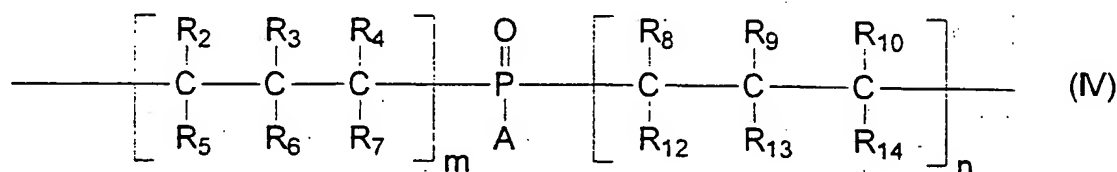
A preferred class of compounds are phosphinatobis(propane-1,2,3-tricarboxylic acid) and the sodium salt thereof of formula (II) and oligomers thereof and phosphinatopropane-1,2,3-tricarboxylic acid and the sodium salt thereof of formula (III) and oligomers thereof



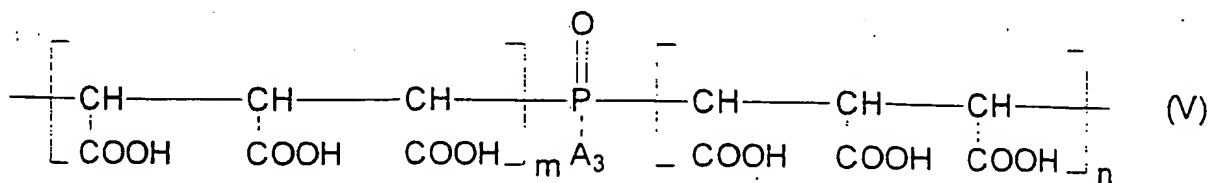
wherein A_1 and A_2 are each independently OH or ONa.

5

Among the oligomers of the compounds of formula (I) there may be mentioned oligomers of formula (IV).

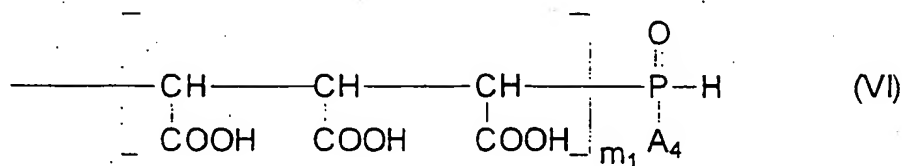


wherein $R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, R_{10}, R_{12}, R_{13}, R_{14}$ and A are as defined for formula (I) and m and n are each independently a small whole numeral and m plus n is greater than 2. A preferred group of oligomers are oligomers of formula (IV) in which R_2, R_3, R_4, R_8, R_9 and R_{10} are each H; $R_5, R_6, R_7, R_{12}, R_{13}$ and R_{14} are each COOM_1 where M_1 is H resulting in an oligomer of formula (V)



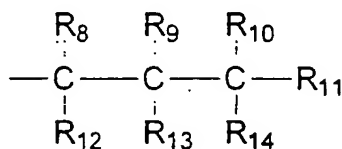
15 where m and n are as defined for formula (IV) and A_3 is OH or ONa.

Another group of oligomers of the compounds of formula (I) are oligomers of formula (VI)

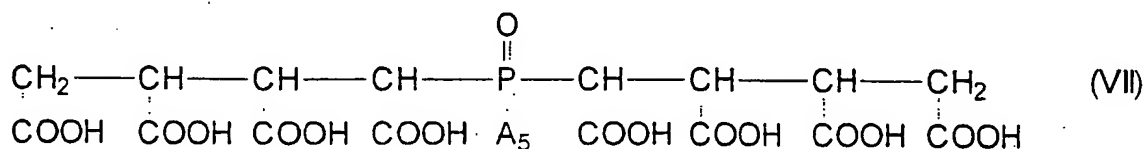


5 wherein A_4 is OH or ONa and m_1 is a small whole number equal to or greater than 2.

Another crosslinking agent within the scope of formula (I) is wherein R is

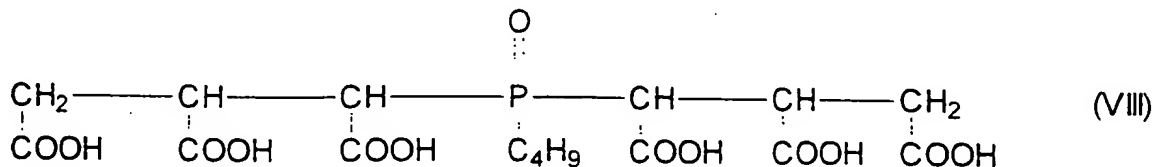


10 and $R_5, R_6, R_7, R_{12}, R_{13}$ and R_{14} are each COOM_1 where M_1 is H; R_1 and R_{11} are each $-\text{CH}_2\text{COOM}$ wherein M is H; R_2, R_3, R_4, R_8, R_9 and R_{10} are each H and A is OH, namely phosphinatobis(butane-1,2,3,4-tetracarboxylic acid) or the sodium salt thereof of formula (VII),



where A_5 is OH or ONa.

15 A still further class of crosslinking agents within the scope of formula (I) are $C_1 - C_8$ alkyl, cyclohexyl or arylbis(polycarboxyalkyl)phosphine oxides, such as butylbis(1,2,3-tricarboxypropyl)phosphine oxide of formula (VIII),



Compounds of formula (I) can be prepared by any suitable process, such as for example, by reacting an unsaturated acid such as prop-1-ene-1,2,3-tricarboxylic acid or but-1-ene-1,2,3,4-tetracarboxylic acid or derivatives thereof with hypophosphorous acid or an alkali metal or ammonium hypophosphite or an alkyl-, cyclohexyl-, or arylphosphine, or phosphine oxide under recognized appropriate conditions of stoichiometry, pH, temperature and free radical initiators. As examples of suitable free radical initiator, there may be mentioned persulfates such as sodium or ammonium persulfates, t-butyl hydroperoxide and other similar free radical initiators.

A process for finishing cellulosic materials, such as textiles or fabrics, is provided by employing one or more of the compounds of formula (I) and oligomers thereof and a curing catalyst in a finishing bath to treat the cellulosic material so that the cellulosic material is impregnated with the crosslinking agents of this invention. In general, the finishing bath will be a solvent solution, preferably an aqueous solution, containing a wrinkle free-providing effective amount of a crosslinking agent of this invention and a curing catalyst. Generally, the finishing bath will contain from about 2 to about 20%, preferably from about 5 to about 15% by weight of crosslinking agents, and from about 0.5 to about 10%, preferably from about 3 to about 8% by weight of curing catalyst. The finishing solution may have other suitable ingredients or agents present, such as for example, a fabric softener, solvents, wetting agents, buffers or the like. The pH of the finishing bath will generally be about pH 2 to pH 4.

In general, the cellulosic material is impregnated with the crosslinking agent and curing catalyst by immersing the cellulosic material in the finishing bath. After the cellulosic material is thoroughly wet in the finishing bath, the cellulosic material is passed between squeeze rolls to remove excess liquid. The cellulosic material is then preferably dried followed by curing in a suitable oven at a temperature of generally from about 150 to 250°C for a period of generally up to about 15 minutes, preferably about 1 to 5 minutes, to cause crosslinking of the cellulosic material to occur. If desired, the

crosslinked cellulosic material may be subsequently given a rinse to remove unreacted crosslinking agent and curing catalyst, and then redried.

The crosslinking agents of this invention can be employed to finish any suitable cellulosic material, generally any material containing about 25% or more cellulosic fibers, such as cotton, flax, jute, hemp, ramie, and regenerated unsubstituted wood cellulosic, such as rayon. The cellulosic material can be, for example, in the form of woven and nonwoven textiles, such as yarns, knit fabrics, or fibers, linters, rovings, slivers and the like.

The invention is illustrated, but not limited, by the following examples.

Preparation of crosslinking agents of this invention is illustrated by Examples 1 and 2.

Example 1

Synthesis of Phosphinatopropane-1,2,3-tricarboxylic Acid and Oligomers

522 g (3 moles) of trans-Aconitic acid (trans-prop-1-ene-1,2,3-tricarboxylic acid) is dissolved in 500 g of water under agitation at about 70°C. To the solution is then added 300 g (2.83 moles) of sodium hypophosphite monohydrate under continuous agitation. Temperature is maintained at 70°C. A solution of 75 g (0.32 mole) of sodium persulfate dissolved in 150 g of water is introduced over a period of 7 hours into the reaction mixture kept agitated at 70°C. After the addition is complete, the reaction is allowed to continue for another 8 hours at 70°C. It is then cooled down to ambient temperature. Reaction results in 1540 g of a slightly colored clear aqueous solution. The solution contains 2.83 moles of monosodium phosphinato(propene-1,2,3-tricarboxylic acid) and its oligomers. ¹³C and ³¹P nmr spectra of the solution confirmed the presence of isomeric phosphinato(propene-1,2,3-tricarboxylic acid).

Example 2

5 **Reaction of Aconitic Acid with Sodium Hypophosphite in Presence of t-Butyl Hydroperoxide**

87 g (0.5 mole) of trans-Aconitic acid (trans-prop-1-ene-1,2,3-tricarboxylic acid) is dissolved in 200 g of water under agitation at about 70°C. The pH of the solution is then increased to about 7 by adding 85 g (0.69 mole) of sodium carbonate monohydrate. 25 g (0.24 mole) of sodium hypophosphite monohydrate is added to the solution while maintaining agitation. The solution temperature is then raised to about 85°C. 30 g of a 70% aqueous solution of t-butyl hydroperoxide is then introduced into the reaction mixture. The reaction is allowed to continue for another 8 hours under stirring at 85°C. The reaction mixture is then cooled down to ambient temperature. t-Butyl alcohol formed in the reaction, any unreacted t-butyl hydroperoxide and part of water are removed from the reaction mixture by distillation under reduced pressure. This process yielded a slightly colored and partially viscous solution. Analysis of the solution indicated that it is a mixture of sodium salts of isomeric phosphinato(propane-1,2,3-tricarboxylic acid), their oligomers, isomeric phosphinatobis(propane-1,2,3-tricarboxylic acid), their oligomers and isomeric phosphonatopropene-1,2,3-tricarboxylic acid.

Example 3

When 100% cotton fabric is impregnated with the crosslinking agents of Examples 1 and 2 using sodium hypophosphite as a curing catalyst improved wrinkle resistant and iron free fabric is obtained.

A typical crosslinking experiment is completed as follows: A finishing bath is prepared by mixing the following: water 81%, crosslinking agents 8% (based on dry solids weight), ten percent aqueous solution of TergitolTM TMN 6 1 % (wetting agent), twentyfive percent aqueous solution of MykronTM HD 2% (softening agent), twenty
5 percent aqueous solution of SilfinTM WHP 4% (finishing agent) and sodium hypophosphite monohydrate 4% (curing catalyst).

The cellulosic material is impregnated with the finishing bath solution to a desired wet weight pickup, dried and followed by curing in a suitable oven at a
10 temperature of 150 to 250⁰ C for a period of 15 minutes, preferably 1 to 5 minutes.

Control Experiment

A control experiment was carried out employing a finishing bath containing
15 all ingredients but the crosslinking agents of examples 1 and 2.

The test swatches were washed, dried and conditioned according to the protocol AATCC 135-95.

20 Durable Press (DP) Rating of fabric crosslinked with the crosslinking agents of this invention was determined according to test protocol AATCC 124-96 which produced the following results

Fabric Crosslinking Compounds	DP Rating
Example 1 Compound	3.3
Example 2 Compound	3.1
Blank control	2.2

Shrinkage of fabric crosslinked with the crosslinking agents of this invention was determined by measuring dimensional changes utilizing the test protocol of AATCC 135-95, with the following results.

5	Fabric Crosslinking Compounds	Average dimensional change %	
		Warp	Fill
	Example 1 Compound	-3.7	-0.7
	Example 2 Compound	-4.8	-1.0
	Blank Control	-9.3	-2.2

10

Tensile strength of fabric crosslinked with the crosslinking agents of this invention was determined determined utilizing the test protocol of ASTM 5034-95, with the following results.

15	Fabric Crosslinking Compounds	Average tensile strength (GRAB)	
		Warp	Fill
	Example 1 Compound	96.56	59.77
	Example 2 Compound	98.37	59.72
	Blank Control	141.86	87.61

20

Tear strength of fabric crosslinked with the crosslinking agents of this invention was determined utilizing the test protocol of ASTM 1424-96, with the following results.

25	Fabric Crosslinking Compounds	Average tear strength	
		Warp	Fill
	Example 1 Compound	3.86	3.56
	Example 2 Compound	3.95	4.18
	Blank Control	6.91	7.53

30

The whiteness index of fabric crosslinked with the crosslinking agents of this invention was measured on an UltrascanTM XE spectrophotometer (space) from Hunter Laboratories, with the following results.

5	Fabric Crosslinking Compounds	Whiteness index, %	
		Before washing	After 5 washings
	Example 1 Compound	49.23	63.53
	Example 2 Compound	55.79	65.26
	Blank Control	55.90	not available

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While the novel compounds of this invention are particularly useful as crosslinking agents for cellulosic materials, particularly for use in the cotton durable press process, they would also be useful as water-treatment chemicals, extractants for metal ions and the like.

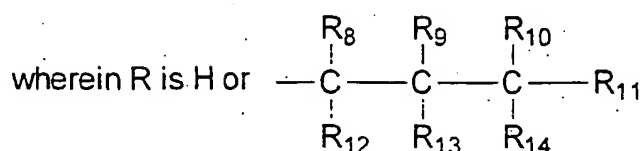
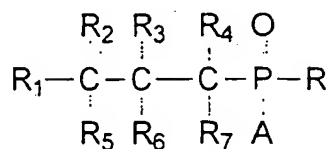
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With the foregoing description of the invention, those skilled in the art will appreciate that modifications may be made to the invention without departing from the spirit thereof. Therefore, it is not intended that the scope of the invention be limited to the specific embodiments illustrated and described.

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We claim:

1. A compound of formula or oligomers thereof



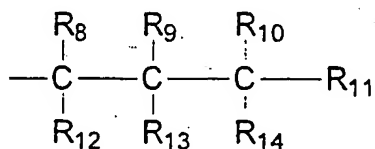
R_1 and R_{11} are each independently H, C_1 to C_4 alkyl and $-CH_2COOM$ in which M is H, Na, K or NH_4 ;

R_2 , R_3 , R_4 , R_8 , R_9 and R_{10} are each independently H or C_1 to C_4 alkyl;

R_5 , R_6 , R_7 , R_{12} , R_{13} and R_{14} are each $COOM_1$ in which M_1 is H, Na, K, or NH_4 , preferably H or Na; and

A is OH, H, C_1 to C_8 alkyl, cyclohexyl, aryl or OM_2 in which M_2 is H, Na, K or NH_4 .

2. A compound of Claim 1 wherein A is OH; R is

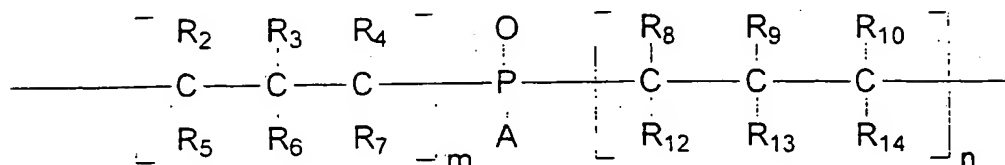


R_1 , R_2 , R_3 , R_4 , R_8 , R_9 , R_{10} and R_{11} are each H; and

R_5 , R_6 , R_7 , R_{11} , R_{12} , R_{13} and R_{14} are each $COOM_1$ where M_1 is H.

3. A compound of Claim 1 wherein A is OH or ONa; R , R_1 , R_2 , R_3 and R_4 are each H; and R_5 , R_6 and R_7 are each $COOM_1$ where M_1 is H.

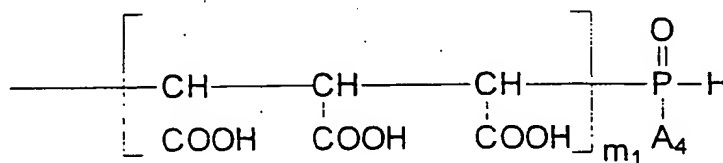
4. A compound of Claim 1 which is an oligomer of the formula



wherein $R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, R_{10}, R_{12}, R_{13}, R_{14}$ and A are as in Claim 1 and m and n are each independently a small whole numeral and m plus n is greater than 2.

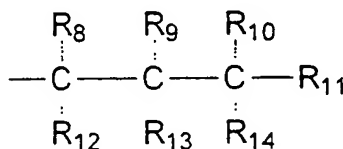
5. A compound of Claim 4 wherein R_2, R_3, R_4, R_8, R_9 and R_{10} are each H; $R_5, R_6, R_7, R_{12}, R_{13}$ and R_{14} are each COOM_1 where M_1 is H; and A is OH or Na.

6. A compound of Claim 1 which is an oligomer of the formula



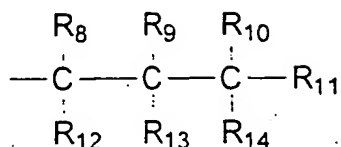
wherein A_4 is OH or ONa and m_1 is a small whole number equal to or greater than 2.

7. A compound of Claim 1 wherein R is



$R_5, R_6, R_7, R_{12}, R_{13}$ and R_{14} are each COOM_1 where M_1 is H; R_1 and R_{11} are each $-\text{CH}_2\text{COOM}$ where M is H, and R_2, R_3, R_4, R_8, R_9 and R_{10} are each H and A is OH or ONa.

8. A compound of Claim 1 wherein R is



A is C₁ – C₈ alkyl, cyclohexyl and aryl; R₁, R₂, R₃, R₄, R₈, R₉, R₁₀ and R₁₁ are each H; and R₅, R₆, R₇, R₁₂, R₁₃ and R₁₄ are each COOM₁ where M₁ is H.

9. A process for treating a cellulosic material to impart wrinkle resistant properties to the material, the process comprising impregnating the cellulosic material with a crosslinking agent and a curing catalyst and curing the cellulosic material, wherein the crosslinking agent comprises at least one compound or oligomer of Claim 1.
10. A process for treating a cellulosic material to impart wrinkle resistant properties to the material, the process comprising impregnating the cellulosic material with a crosslinking agent and a curing catalyst and curing the cellulosic material, wherein the crosslinking agent comprises at least one compound of Claim 2.
11. A process for treating a cellulosic material to impart wrinkle resistant properties to the material, the process comprising impregnating the cellulosic material with a crosslinking agent and a curing catalyst and curing the cellulosic material, wherein the crosslinking agent comprises at least one compound of Claim 3.
12. A process for treating a cellulosic material to impart wrinkle resistant properties to the material, the process comprising impregnating the cellulosic material with a crosslinking agent and a curing catalyst and curing the cellulosic material, wherein the crosslinking agent comprises at least one oligomer of Claim 4.
13. A process for treating a cellulosic material to impart wrinkle resistant properties to the material, the process comprising impregnating the cellulosic material with a

crosslinking agent and a curing catalyst and curing the cellulosic material, wherein the crosslinking agent comprises at least one oligomer of Claim 5.

14. A process for treating a cellulosic material to impart wrinkle resistant properties to the material, the process comprising impregnating the cellulosic material with a crosslinking agent and a curing catalyst and curing the cellulosic material, wherein the crosslinking agent comprises at least one compound of Claim 6.
15. A process for treating a cellulosic material to impart wrinkle resistant properties to the material, the process comprising impregnating the cellulosic material with a crosslinking agent and a curing catalyst and curing the cellulosic material, wherein the crosslinking agent comprises at least one compound of Claim 7.
16. A process for treating a cellulosic material to impart wrinkle resistant properties to the material, the process comprising impregnating the cellulosic material with a crosslinking agent and a curing catalyst and curing the cellulosic material, wherein the crosslinking agent comprises at least one compound of Claim 8.

INTERNATIONAL SEARCH REPORT

Internat Application No

PCT/US 01/00788

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07F9/30 C07F9/53 D06M13/285

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07F D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 454 323 A (NALCO CHEMICAL CO.) 30 October 1991 (1991-10-30) the whole document	1,4,5
X	US 5 018 577 A (JERRY E. PARDUE) 28 May 1991 (1991-05-28) the whole document	1,4,5
Y	US 5 273 549 A (WILHELM DIDIER) 28 December 1993 (1993-12-28) the whole document	1,9-16
Y	US 5 496 476 A (ROBERT H. TANG) 5 March 1996 (1996-03-05) the whole document	1,9-16



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

6 April 2001

Date of mailing of the international search report

27/04/2001

Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/00788

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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